Growth of TeO$_2$ single crystals by the low temperature gradient Czochralski method with nonuniform heating

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A B S T R A C T

A growth station for growing paratellurite single crystals is presented. Modification of Czochralski furnace consists of nonuniform heating of melt by remaining low temperature gradients near the front of crystallization. It is supposed that local overheating of the lower parts of the melt breaks particle associates in the melt. This assumption is confirmed by the growth of bubble-free TeO$_2$ crystals weighting up to 1.8 kg.

1. Introduction

Paratellurite (TeO$_2$) crystals are widely used in acusto-optics in the range of 0.35–5 µm and as a birefringent element in the near IR range [1,2]. Paratellurite melts congruently at 734°C and crystallizes in P$_{42}$$\bar{2}$ space group without any phase transitions at lower temperature. The most efficient way to grow TeO$_2$ crystals is the Czochralski method [3–5], however, the Bridgman growth was also reported [6,7].

The growth of TeO$_2$ crystals by the Czochralski method in [110] direction under high-gradient temperature conditions (about 10$^3$ /cm) leads to the formation of nonfaceted crystals with a rounded section (Fig. 1). Typical defects of these crystals are the relatively high density of dislocations (about 10$^3$–10$^4$ cm$^{-2}$ and more) and high residual thermoelastic stresses, which are characterized by induced optical biaxiality, especially in the peripheral part of crystals (Fig. 1b,c). Normally, only the middle parts of high-gradient crystals are of high acusto-optic quality and without thermoelastic stress.

The growth of TeO$_2$ crystals by the Czochralski method also in [110] direction but under low-gradient thermal conditions (1–2 /cm) allows producing faceted crystals (Fig. 2a–c) with low thermoelastic stresses (Fig. 2d) and high optical homogeneity [8]. The density of dislocations decreases 1–2 orders. The horizontal section of crystals becomes polygonal (Fig. 2b,c) while the lateral surface of boules reveals two faces of a tetragonal prism (110), and at certain growth parameters it is possible to grow crystals with a flat crystallization front totally shaped by the face of prism (110) (Fig. 2c).

However crystals grown by this method have accumulations of bubble inclusions (Fig. 2a) and the so-called “hair-like” scattering (Fig. 2e) which considerably decrease yield of crystals both for acousto-optic and polarizers applications. It is known that elementary tellurium may appear in the melt as a result of reaction between TeO$_2$ and Pt crucible [9]. Also Pt is contaminated by melt if iron impurity occurs in TeO$_2$ [10]. On the other hand, entrapment of bubbles by growing TeO$_2$ is attributed to the peculiarities of melt flow structure [11].

Results of our chemical analyses evidence that bubbles and scattering are not directly related to the impurity inhomogeneity of the crystals. These defects were observed in the crystals after the first growth from high purity synthesized TeO$_2$ in the acid-cleaned Pt crucible. It is worth noting that TeO$_2$ melt tends to polymerization [12]. Hence the difference of crystal quality is likely to be caused by changes in the melt structure. Under low temperature gradient a larger portion of the melt is subjected to association. The accumulation of such associates near the crystallization front increases melt viscosity, which makes trapping of bubbles easier, and incorporation of “bulk” associates into the structure may result in low-angle mismatches on a nanoscale [13].
The latter is revealed in the local variations of refractive indices and, as a result, in the occurrence of “hair-like” scattering in paratellurite crystals.

In high gradient approach the melt is constantly mixed through the high temperature region where the associates are broken. This is supposed to be a cause of less occurrence of bubbles in “high gradient” crystals. In turn, “hair-like” scattering is observed in case of impure melt.

Thus, an idea to grow high quality TeO₂ crystals consists in combination of low temperature gradient conditions at the front of crystallization in order to avoid thermal stresses. And on the other hand, to maintain some local overheating away from the melt surface to decrease the size of growth units. In this work we present the design of the modified Czochralski furnace for crystal growth of TeO₂ crystals in low temperature gradient conditions with nonuniform heating.

2. Growth station

The station is equipped with the distributed system of automatic control of the crystal-cross section [14]. A control algorithm implements the adjustment of furnace temperature according to the difference between signal of the weight sensor at bottom position and program weight. The crystal is moved by means of pulling and rotating the crystal holder.

The heating furnace consists of four vertical zones (Top, Middle, Lower and Bottom), the Top and Bottom are made of single heaters, while each of the Middle and Lower zones comprise three heating segments (Fig. 3a). Thus, the total number of heating elements equals eight. All heating elements are connected serially and each one is in a parallel connection to a power solid state relay which is controlled by the load commutator. If any relay is switched on, the corresponding heater becomes short-circuited.
The feedback signal for thermoregulator is provided by three parallely connected thermocouples placed around Middle zone. So the temperature inside the furnace is controlled by only one thermoregulator. The required temperature distribution in the furnace is achieved by selecting the cyclic program with commutation times of the heating elements.

This design of the furnace and control system makes it possible to adjust axial temperature gradient as well as to create nonuniform radial temperature distribution on the level of Middle and Lower zones.

3. Growth experiments

Tellurium dioxide of purity 99.998% was used as the starting charge. The initial melt was 2.5 kg in weight and filled ~70 mm height of crucible 100 mm in diameter. Seeding was carried out in axisymmetric low gradient heat field at the commutation time of the heating elements shown on the diagram in Fig. 3d. Distributions of temperature along the central axis and at the periphery nearby the heaters (X, Y and Z directions, see Fig. 3b) are shown by dotted curves in Fig. 3c. Crystal pulling and rotating rates were 3–5 mm/day and 13–15 rpm, respectively.

As the conical part of crystal grew, the times of switching of the heating elements were gradually changed at the rate of /C240.5 s/day to the values indicated in Fig. 3e. In spite of the change in the temperature distribution during growth, the thermal balance was well handled by cross-section control system. Temperature distribution in the center and in the periphery is represented by solid curves in Fig. 3c. Thus, in the lower part of the growth crucible along the X direction the conditions of relative overheating were created. While along Y, Z and central axis a certain decrease of temperature was found.

The temperature distributions at Fig. 3c were obtained by uncovered Pt-Pt/10%Rh thermocouple without growing crystal. The measurements illustrate qualitative and quantitative difference between axisymmetric and nonuniform heating of the crucible.

In a number of experiments paratellurite crystals weighing 1 to 1.8 kg fully free from bubble inclusions were grown (Fig. 4). So, it may be supposed that partial overheating results in a decrease of particle associates in the melt which in turn is likely to be the reason for the absence of bubbles in the crystals. On the other hand, the well faceted shape of the crystals suggests that low-gradient thermal conditions near the front of crystallization remained. In order to increase the nonuniformity of heating the switching delays for heaters 6–7 and 8 were increased up to 7 and 8 s, respectively. Nevertheless, “hair-like” scattering was still observed. In spite of that fact, optical quality of the crystals satisfied the standard of birefringent material in commercial polarizers.

4. Conclusions

A growth station for automatic growth of paratellurite single crystals under the conditions of nonuniform heating is presented.
The Czochralski method was modified in order to create overheated region in the melt, while low temperature gradient conditions near the front of crystallization were remained in order to prevent thermoelastic stress in the crystal. The resulting TeO₂ crystals were found to be bubble free and of high optical homogeneity.

Polymerization of TeO₂ melt is likely to play an important role in the quality of grown crystals. We assume that in our experiments the melt associates decompose when they convectively move through the region of melt with a higher temperature and the crystal grows statistically from smaller “building” particles. As a result, the improved Czochralski technique have provided sufficient increment of crystal yield for production of TeO₂ polarizers.

References